Charge Transfer Reactions of Organic Ions Containing Oxygen:

Correlation Between Reaction Energetics and Cross Sections

G. C. Shields, P. A. Steiner IV, P. R. Nelson, M. C. Trauner† and T. F. Moran

School of Chemistry and †Office of Computing Services, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

Cross sections for charge transfer reactions of organic ions containing oxygen have been obtained using time-of-flight techniques. Charge transfer cross sections have been determined for reactions of 2.0 to 3.4 keV ions produced by electron impact ionization of oxygen containing molecules such as methanol, ethanal and ethanol. Experimental cross section magnitudes have been correlated with reaction energy defects computed from ion recombination energies and target ionization energies. Large cross sections are observed for reacting systems with small energy defects.

INTRODUCTION

Electron impact ionization produces a molecular ion by means of a vertical Franck-Condon transition in which the ion is formed initially in the nuclear configuration of the neutral molecule. This ion may be electronically excited and undergo a spontaneous radiative transition¹ to a lower electronic state, or it may rearrange or fragment before leaving the ion source. All these ions are accelerated to keV energies and can undergo charge transfer reactions with target molecules. Charge transfer interactions of keV ions with target molecules occur in time periods short compared to nuclear motion, with the result that fast neutral products initially possess the structures of the reactant ions. For a symmetric, resonant, charge transfer process of the type

in which ions and molecules have the same configuration, the recombination energy (energy released by neutralization of the fast ion) exactly balances the ionization potential of the slow target molecule and large cross sections are expected. However, the reactions involving incident ions of the same mass as shown in (1) but possessing different structures may not be resonant. Such a possibility is illustrated by the reaction

The energetics of reactions (1) and (2) differ since the recombination energy of $[\text{HCOH}]^{+*}$ is less than that of $[\text{H}_2\text{CO}]^{+*}$. Since recombination energies are dependent on ion structures, each reaction involving a different ion structure with a given target molecule will have a distinct energy defect. Reaction energy defects, Q , have been determined from the differences between ionization energies and recombination energies computed by using

semi-empirical self-consistent field molecular orbital methods. Time-of-flight techniques have been utilized to measure charge transfer cross sections for reactant ions produced by electron impact ionization of oxygen containing molecules. The present study examines the relationship between the magnitude of experimental charge transfer cross sections and reaction energy defects.

EXPERIMENTAL

Time-of-flight techniques were employed to measure² fast neutral products resulting from keV charge transfer reactions. The apparatus and techniques have been used previously to monitor fast neutral products formed from charge transfer reactions of singly² and doubly³ charged ions. Reactant molecular ions and their characteristic fragment ions were produced by controlled electron impact ionization of neutral molecules. Ionizing electrons were emitted from a directly heated filament and accelerated into the ion source by a voltage controllable from 2 to 100 eV. The electron beam intensity was kept constant throughout each measurement with a regulated filament current supply.

Reactant molecular and fragment ions produced by electron impact were drawn out of the source by a fast rising pulse and accelerated to terminal velocities. The fully accelerated ion beam entered a static gas collision region where ion-molecule interactions were possible. Unreacted ions and fast neutral products from charge transfer reactions proceeded through a one meter drift region and were collected on the cathode of a gated electron multiplier. The final 0.2 m segment of drift region was insulated from the first segment in order to retard the ions as they passed from the first drift region to the second. Application of a deceleration voltage to the second region resulted in longer arrival times for ions than for fast neutral products with the same initial mass and velocity. For each ion peak present in a mass

spectrum, a corresponding neutral peak from charge transfer was detected as well.

The number of secondary electrons emitted from metal surfaces by high-energy particle bombardment has been found to be equivalent for both the ion M^+ and the charge transfer neutral product M^0 .^{4,5} Equal emission coefficients resulted in equivalent electron multiplier response for both the incident ion and its corresponding neutral product at 3 keV. The well documented Ar^+-Ar charge transfer cross sections⁶ have been employed to calibrate³ the time-of-flight system over the accelerating voltage range of 2.0–3.4 keV.

RESULTS AND DISCUSSION

Numerous investigations of organic ions containing oxygen have been undertaken, but much remains to be learned about the energies, structures and reactivities of these ions. A review article by Holmes⁷ points out that the two primary experimental methods for assigning structures to gas phase ions involve ion thermochemistry and ion dissociation characteristics. Thus, the bulk of available data consists of experimentally determined ionic heats of formation along with collisional activation studies of ion structures. Examination of ion reactivity is a less widely used approach to obtain information about atomic locations in ionic molecules. The study of ion reactivity in charge transfer reactions also provides another possible method to obtain information about gas phase ions. Ion reactivities are quantitatively determined by the magnitudes of reaction cross sections.

Cross sections for charge transfer involving ions reacting with methanol target molecules are displayed in Fig. 1 as a function of ion kinetic energy (keV). Reaction cross sections in this figure are given for m/z 15, 29, 30, 31, 32 and 33 which are the dominant ions produced by electron impact ionization of methanol. The $[M+1]^+$ ion peak formed from bimolecular ion-molecule reactions in the ion source has been corrected for the M^+ isotope component. Cross sections displayed in Fig. 1 are in the range of 2–18 Å². For each reaction, there is a slight increase in the cross section as a function of

Table 1. Charge transfer cross sections and energy defects for ions reacting with CH₃OH target molecules

Reactant ion m/z	Ion structure	MINDO/3 ion recombination energy (eV)	Q (eV)	Cross section Å ² at 3 keV
15	$[CH_3]^+$	9.40	-1.54	14
29	$[HCO]^+$	7.03	-3.91	7
	$[COH]^+$	6.41	-4.53	
30	$[HCOH]^+$	7.84	-3.10	16
	$[CH_2O]^+$	10.54	-0.40	
31	$[CH_2OH]^+$	7.20	-3.74	4
	$[CH_3O]^+$	8.32	-2.62	
32	$[CH_3OH]^+$	9.65	-1.29	16
	$[CH_2OH_2]^+$	6.77	-4.17	
33	$[CH_3OH_2]^+$	6.51	-4.43	3

increasing ion kinetic energy. This behavior is characteristic of non-resonant charge transfer reactions.⁸

In order to relate measured cross sections to reaction energy defects it is necessary to determine the energy liberated when an electron recombines with the reactant ion. These ionic recombination energies have been obtained with the aid of the MINDO/3 semi-empirical SCF-MO approach using techniques outlined previously.⁹ Individual incident ion neutralization and target ionization 'half reactions' occur as vertical Franck-Condon transitions since electron transfer processes take place in time periods short compared with nuclear motion. Consequently, each recombination energy has been determined by calculating the energy difference between the reactant ion structure and the neutral product 'frozen' in the configuration of the incident ion. This data is reported in Table 1 for major ions produced by electron impact ionization of methanol. Ions listed in this table have received support from experimental and theoretical investigations designed to ascertain their structural configuration.

Reactions of $[CH_3OH_2]^+$ ions with methanol have the smallest charge transfer cross section of all the ions illustrated in Fig. 1, which is not surprising in view of the large (-4.43 eV) energy defect given in Table 1 for this reaction. This energy defect is expected to be reasonably accurate since the MINDO/3 heat of formation of 5.92 eV is in agreement with the accepted value of 5.96 eV for $[CH_3OH_2]^+$ reported by Nobes and Radom.¹⁰

The conventional $[CH_3OH]^+$ molecular M^+ ion has been reported to be the structure formed by electron impact of methanol.¹¹ As shown in Fig. 1 and Table 1 this ion has a larger (16 Å²) reaction cross section and smaller (-1.29 eV) energy defect than the corresponding reactions of $[M+1]^+$ ions. A non-conventional $[CH_2OH_2]^+$ isomer has been reported^{11–13} as a fragment ion from ionic decompositions of higher molecular weight molecules such as glycol.¹³ Although this $[CH_2OH_2]^+$ isomer has a lower energy¹² than $[CH_3OH]^+$, there is a high barrier to isomerization and the two isomers do not interconvert.¹¹ As a result we expect the dominant ion at m/z 32 in our reactant ion beam to possess the $[CH_3OH]^+$ structure.

Both collisional activation experiments¹⁴ and theoretical investigations^{14,15} have indicated that stable m/z 31 ions formed from ionization of methanol at high and low electron energies have the $[CH_2OH]^+$ structure.

Figure 1. Charge transfer cross sections (10^{-16} cm²) presented as a function of ion kinetic energy (keV). Reactant keV ions produced by electron impact ionization of methanol undergo charge exchange reactions with neutral methanol target molecules. Each curve is labelled with the reactant ion m/z .

Collisional activation experiments¹⁴ also indicate that this is the only long-lived ion structure for m/z 31 ions from methanol. The small $4 \text{ \AA}^2$ charge transfer cross section shown in Fig. 1 is consistent with the large -3.74 eV energy defect for reactions of these $[\text{CH}_2\text{OH}]^+$ ions.

The $16 \text{ \AA}^2$ charge transfer cross section for m/z 30 ions is quite large for collisions of $[\text{HCOH}]^{++}$ species since the energy defect for this reaction is -3.10 eV . Reactions involving stable¹⁶ $[\text{H}_2\text{CO}]^{++}$ isomers with an energy defect of only -0.40 eV would be more compatible with our measured cross sections. Photoionization experiments of Berkowitz¹⁷ using deuterated methanol have indicated that the $[\text{HCOH}]^{++}$ isomer is formed exclusively near threshold and that both $[\text{HCOH}]^{++}$ and $[\text{H}_2\text{CO}]^{++}$ isomers are formed at high photon energies. Collisional activation spectra of m/z 30 ions from methanol, obtained by Burgers *et al.*,¹⁸ were consistent with the predominance of $[\text{HCOH}]^{++}$ isomers in their ion beam although they suggest that $[\text{H}_2\text{CO}]^{++}$ ions were undoubtedly present. It is expected that our reactant ion beam is composed of both $[\text{HCOH}]^{++}$ and $[\text{H}_2\text{CO}]^{++}$ ions. Charge transfer processes involving two different reactant species results in a total flux of fast neutral products, $i_p(\text{total})$, given by

$$i_p(\text{total}) = i_{p1} + i_{p2} = f_1 i_R n l \sigma_1 + f_2 i_R n l \sigma_2 \quad (3)$$

where f_1 and f_2 are the fractions of $[\text{HCOH}]^{++}$ and $[\text{H}_2\text{CO}]^{++}$ ions respectively in the reactant ($m/z = 30$) ion beam of total flux i_R . The concentration of neutral target molecules in Eqn (3) is denoted by n and the path length over which reaction occurs is given by l . Individual cross sections are represented by σ_1 and σ_2 for reactants of type 1 and 2 respectively. Equation (3) can be rearranged to the form

$$i_p(\text{total})/i_R n l = \sigma(\text{total}) = f_1 \sigma_1 + f_2 \sigma_2 \quad (4)$$

Relative variation of the total cross section σ is displayed in Fig. 2 as a function of electron energy over the 12 to 100 eV range. At electron energies near threshold for forming $m/z = 30$ ions, the measured relative cross section is approximately 0.4 times the $16 \text{ \AA}^2$ value obtained at 100 eV. In the threshold region where $\sigma = \sigma_1 \approx 6.4 \text{ \AA}^2$, f_1 is equal to unity and f_2 is zero since here only reactant $[\text{HCOH}]^{++}$ ions are produced¹⁷ by electron impact of methanol. However as the ionizing electron energy is

Figure 2. Relative total cross section for charge transfer reactions involving methanol target molecules as a function of ionizing electron energy used to produce the m/z 30 reactant ion beam.

increased above $\sim 17 \text{ eV}$, another state is produced which leads to an increase in the total measured cross section. Data in Fig. 2 show that the fraction, f_2 , of this state increases as the ionizing electron energy is increased and that this component has a cross section σ_2 which is larger than σ_1 . Association of this second component in our m/z 30 ion beam with $[\text{H}_2\text{CO}]^{++}$ structure ions has been indicated in the experiments of Berkowitz¹⁷ which show the exclusive formation of $[\text{HCOH}]^{++}$ between 12 and 17 eV and a mixture of both $[\text{HCOH}]^{++}$ and $[\text{H}_2\text{CO}]^{++}$ ion structures at higher ionizing energies. Data in Fig. 2 giving $\sigma_2 > \sigma_1$ are consistent with information in Table 1 which illustrates energy defects are small for reactions of $[\text{H}_2\text{CO}]^{++}$ but large for $[\text{HCOH}]^{++}$ ions. The exact value of σ_2 cannot be determined from Eqn (4) since the relative isomer abundances f_1 and f_2 are not known quantitatively at high electron energies. The isotopic photoionization data of Ref. 17 suggests $f_1 \approx f_2$, however the collisional activation spectra of Burgers *et al.*¹⁸ are consistent with $f_1 \geq f_2$.

In order to determine the magnitude of σ_2 we have employed reactant ions from electron impact of formaldehyde vapor, where both collisional activation^{18,19} and ESR²⁰ experiments indicate the m/z 30 ions possess the $[\text{H}_2\text{CO}]^{++}$ structure. Our measured 3 keV charge transfer cross sections of $62 \text{ \AA}^2$ for exclusive formaldehyde $[\text{H}_2\text{CO}]^{++}$ ion reactions, along with values of $\sigma_1 \approx 6.4 \text{ \AA}^2$ and $\sigma(\text{total}) = 16 \text{ \AA}^2$ from the methanol derived m/z 30 ions enable f_1 and f_2 to be determined from Eqn (4). With the aid of this information we estimate the relative abundance of $[\text{HCOH}]^{++}$ ions, f_1 , to be 83% when produced from high energy electron impact ionization of methanol.

Charge transfer cross sections shown in Fig. 1 for m/z 29 ions are small and consistent with large energy defects shown in Table 1 for this reaction. Previous experiments^{17,21,22} have shown both $[\text{HCO}]^+$ and $[\text{COH}]^+$ are formed from ionization of methanol but $[\text{HCO}]^+$ is the most abundant species. However, both these species have large energy defects and each reactant ion is expected to result in a small cross section which makes studies of individual isomer ions of this type difficult by charge transfer techniques.

Correlation between reaction energy defects and charge transfer cross sections is displayed in Fig. 3. The open circles give the data listed in Table 1. Numbers next to each point indicate m/z of the reactant ion. Closed triangles illustrate the small cross sections obtained for charge transfer in $[\text{CH}_3\text{OH}]^+ + \text{Ar}$ and $[\text{CH}_3]^+ + \text{Ar}$ systems where energy defects are greater than -6 eV . Closed circles represent cross sections obtained by Kir'yakov *et al.*²³ for reactions of $[\text{CH}_3\text{OH}]^+$, $[\text{CH}_2\text{OH}]^+$, $[\text{CH}_3\text{O}]^+$, $[\text{CH}_2\text{O}]^+$ and $([\text{COH}]^+, [\text{HCO}]^+)$ ions with neutral magnesium. Cross sections obtained by these investigations²³ at lower energies were extrapolated to 3 keV using the $\sigma^{1/2}$ vs $\log E$ plot characteristics of the data in Ref. 23. The data with Mg as the neutral target is particularly useful since both positive and negative energy defects are encompassed. The m/z 30 solid point in Fig. 3 represents the average energy defect for several available exothermic reaction pathways. Open triangles are data for reactions of $[\text{CH}_3\text{OCH}_3]^+$ and $[\text{CH}_3]^+$ ions with dimethyl ether. Data in Fig. 3 illustrate the strong dependence of charge

Figure 3. Charge transfer cross sections (10^{-16} cm^2) presented as a function of reaction energy defects (eV). Data points are labelled by the reactant ion m/z value. Open circles, open triangles, closed triangles and closed circles represent data for reactions involving neutral methanol, dimethyl ether, argon and magnesium (Ref. 23) respectively.

Figure 4. Charge transfer cross sections (10^{-16} cm^2) presented as a function of ion kinetic energy (keV). Reactant keV ions produced by electron impact ionization of ethanal undergo charge exchange reactions with neutral ethanal target molecules. Each curve is labelled with the reactant ion m/z value.

transfer cross section on reaction energy defect especially as these energy deficits approach zero where close energy balance exists between reactant and product channels.

Charge transfer cross sections for reactions of ions with ethanal target molecules are displayed in Fig. 4 as a function of ion kinetic energy. Incident ions in these

Table 2. Charge transfer cross sections and energy defects for ions reacting with CH_3CHO target molecules

Reactant ion m/z	Ion structure	MINDO/3 ion recombination energy (eV)	Q (eV)	Cross section $\text{\AA}^2$ at 3 keV
29	$[\text{HCO}]^+$	7.03	-3.23	11
	$[\text{COH}]^+$	6.41	-3.85	
42	$[\text{CH}_2\text{CO}]^{++}$	8.50	-1.76	23
43	$[\text{CH}_3\text{CO}]^+$	6.32	-3.94	10
44	$[\text{CH}_3\text{CHO}]^{++}$	9.41	-0.85	31
45	$[\text{CH}_3\text{CHOH}]^+$	6.75	-3.51	9

Figure 5. Charge transfer cross sections (10^{-16} cm^2) presented as a function of ion kinetic energy (keV). Reactant keV ions produced by electron impact ionization of ethanol undergo charge exchange reactions with neutral ethanol target molecules. Each curve is labeled with the reactant ion m/z value.

reactions were produced by the electron impact ionization of ethanal. Individual points displayed for m/z 42 illustrate typical data taken at 0.2 keV intervals. Energy defects are given in Table 2 for this series of reactions. Reaction cross sections involving the molecular ion are the largest of all the different reactant systems shown in Fig. 4, which is not surprising since reactions of $[\text{CH}_3\text{CHO}]^{++}$ ions have the smallest energy defect of all those listed in Table 2. Both metastable ion²⁴ and chemical activation²⁵ studies have shown this molecular ion to possess the $[\text{CH}_3\text{CHO}]^{++}$ configuration for which we estimate a recombination energy of 9.41 eV; a value close to the ionization potential of ethanal. Experimental²⁶⁻²⁸ and theoretical²⁹ investigations have indicated the minimum energy $[\text{CH}_3\text{CO}]^+$ structure to be the dominant²⁸ ($\sim 95\%$) m/z 43 species from ionization of ethanal. This $[\text{CH}_3\text{CO}]^+$ ion has a large energy defect and a relatively small cross section for $[\text{CH}_3\text{CO}]^+ - \text{CH}_3\text{CHO}$ charge transfer reactions.

Cross sections for the corresponding keV reactions of ions from ethanol in Fig. 5 are shown to range from 5

Figure 6. Charge transfer cross sections (10^{-16} cm^2) displayed as a function of reaction energy defects. Open and closed circles represent data for reactions involving neutral ethanol and ethanal target molecules. The solid triangle gives the datum for reactions of m/z 42 with argon.

to $37 \text{ \AA}^2$. Individual points displayed for m/z 42 (solid) and m/z 46 (open) illustrate typical data taken at 0.2 keV intervals over the range of 2.0 to 3.4 keV. Reactant ion recombination energies and energy defects for reactions illustrated in Fig. 5 are given in Table 3. The $20 \text{ \AA}^2$ cross section involving ethanal molecular ions is in line with the -1.57 eV energy defect for $[\text{CH}_3\text{CH}_2\text{OH}]^{++}$ reactions. Although other isomers are known³⁰⁻³³ to be formed in ionization of higher molecular weight precursors, the sophisticated ion neutralization-reionization and collisionally activated dissociation experiments of Ref. 33 have shown that $>95\%$ of m/z 46 ions from ethanol have the $\text{CH}_3\text{CH}_2\text{OH}$ structure.

Charge stripping experiments indicate³⁴ ions of the type $[\text{CH}_3\text{CHOH}]^+$ to be the dominant species in an m/z 45 ion beam from ionization of ethanol. The large energy defect shown in Table 3 for charge transfer reactions of m/z 45 results in a small charge transfer cross section. The dependence between charge transfer cross sections and energy defects for reactions of all the ions listed in Tables 2 and 3 is illustrated in Fig. 6. The overall trend shown in this figure is very similar to that observed in Fig. 3 for the other reactant systems and is indicative that this correlation between cross sections and energy defects is a general feature of charge transfer reactions.

In summary, the magnitudes of charge transfer cross sections are found to be strongly dependent on the size of the reaction energy defects. Small reaction energy defects give rise to large charge transfer cross sections.

Table 3. Charge transfer cross sections and energy defects for ions reacting with $\text{CH}_3\text{CH}_2\text{OH}$ target molecules

Reactant ion m/z	Ion structure	MINDO/3 ion recombination energy (eV)	Q (eV)	Cross section $\text{\AA}^2$ at 3 keV
26	$[\text{C}_2\text{H}_2]^{++}$	10.18	-0.46	34
27	$[\text{C}_2\text{H}_3]^+$	5.69	-4.95	6
29	$[\text{C}_2\text{H}_5]^+$	6.30	-4.34	9
	$[\text{HCO}]^+$	7.03	-3.61	
	$[\text{COH}]^+$	6.41	-4.23	
30	$[\text{HCOH}]^{++}$	7.84	-2.80	16
	$[\text{CH}_2\text{O}]^{++}$	10.54	-0.10	
31	$[\text{CH}_2\text{OH}]^+$	7.20	-3.44	7
42	$[\text{CH}_2\text{CO}]^{++}$	8.50	-2.14	23
43	$[\text{CH}_3\text{CO}]^+$	6.32	-4.32	11
44	$[\text{CH}_3\text{CHO}]^{++}$	9.41	-1.23	36
45	$[\text{CH}_3\text{CHOH}]^+$	6.75	-3.89	9
46	$[\text{CH}_3\text{CH}_2\text{OH}]^{++}$	9.07	-1.57	20
47	$[\text{CH}_3\text{CH}_2\text{OH}_2]^+$	6.25	-4.39	8

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